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MORPHOLOGICAL PROPERTIES OF NANOPOWDERS OF THE SYSTEM $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ AS A FUNCTION OF THE CONDITIONS FOR OBTAINING PRECURSORS

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The morphological properties of powders with the same chemical composition in the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ with the components precipitated in different sequences are investigated. The schemes used to obtain the precursors of this system make it possible to prepare powders with a prescribed chemical composition and high precipitation completeness and with individual particle sizes near 20 nm. The morphology, degree of agglomeration, and porous structure of the synthesized powders depend on the conditions under which the precursors are obtained.

Key words: sol – gel technology, nanopowder, ceramics.

For ceramic materials the dispersity and granulometric composition of the initial powders are not simply size characteristics of the system, but rather they have a defining significance as technological parameters. The question of the need to take account of these parameters in order to obtain slips, intermediate products, and subsequently materials with the required structure was examined in P. O. Gribovskii's works [1]. Since nanopowders are being increasingly used in ceramics technology, questions concerning their producibility are very important [2 – 4].

The possibility of certifying powders using new-generation instrument technology for analyzing the particle-size range and granulometric composition makes it possible to advance validated assumptions and explain the behavior of powders within technological limits. For example, Ukrainian scientists have shown in a publication devoted to powders obtained by a chemical method in the system $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ that the fractal structure of xerogels depends on the sequence in which the components in this system are precipitated [5]; this dependence is reflected in the dimensional characteristics of the powders and affects the technological parameters, specifically, the filtration coefficient.

Our experimental studies of the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ as a basis for high-strength ceramics have shown that

the precipitation sequence of the components affects the thermal-phase formation of precursors with the same chemical composition and grain composition of the microstructure of the ceramic [6, 7].

The objective of the present work is to examine in detail the morphological properties of powders with the same chemical composition which are obtained in the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ with the components precipitated in different sequences.

The following composition was chosen for the present investigations (molar content, %): 50 $\text{Al}_2\text{O}_3 - 50$ (88 $\text{ZrO}_2 + 12 \text{CeO}_2$). Powder precursors were obtained by the sol – gel method, which gives the best results for synthesis of complex oxide ceramic, giving compositions that are homogeneous and pure. Solutions of the following salts were obtained (1M): $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Freshly prepared solutions were used in order to decrease the effect of the hydrolysis of the initial salts. A concentrated water solution of ammonia was used as a precipitator; the surfactant (butanol) was introduced into the solution. The precipitation was performed in 120 min at room temperature. The pH of the medium was maintained in the interval 9.5 – 9.6 to ensure that the precipitation of the components is complete.

Nanopowders were obtained from the precursors by precipitating the components of the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ in different sequences: simultaneously (I) and successively — zirconium and cerium first, then aluminum (II); aluminum first, then zirconium and cerium (III). The primary

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TABLE 1.

Oxide	Mass content in the powders, %			
	theoretical	computed*		
		I	II	III
ZrO ₂	47.0	45.0	45.6	45.2
Al ₂ O ₃	44.0	45.8	45.7	46.2
CeO ₂	9.0	9.2	8.7	8.6

* The error is not more than 2% by mass.

TABLE 2.

Synthesized powder	Crystal lattice parameters of the solid solution		RCS, nm
	<i>a</i> , Å	<i>V</i> , Å ³	
I	5.155	136.97	11.5
II	5.155	137.02	11.8
III	5.157	137.12	11.1
Error, Å	0.001	0.20	

TABLE 3.

Synthesized powder	Specific surface area, m ² /g	Average size of the individual particles, nm
I	66	18
II	61	20
III	69	17

precipitate was obtained in 30 min, and the total duration of the process was the same for all types of precipitation — 120 min. The gel-like precipitates were dried at 180 °C. After drying, the products of precipitation (xerogels) were heat-treated at 950 °C. The following methods were used to study the synthesized materials.

Low-temperature adsorption – desorption was used to measure the specific surface area of the powders obtained (TriStar-3000 adsorption – structural analyzer). The results of the analysis were used to determine the dependence of the volume distribution of the pores on their diameter in the mesopore range. An Analizette-22 laser analyzer was used to obtain the size distribution of the agglomerates. A XRD-6000 diffractometer was used to perform a qualitative analysis of the phase composition of the samples. The Selyakov – Scherrer relation was used to calculate the size of the regions of coherent scattering (RCS). An ULTIMA 2 spectrometer (JOBIN YVON HORIBA Company, France – Japan) was used to determine the elemental composition of the precursors by means of atomic-emission spectrometry with inductively coupled plasma. The relative standard deviation *S_r* did not exceed 0.025 for different elements.

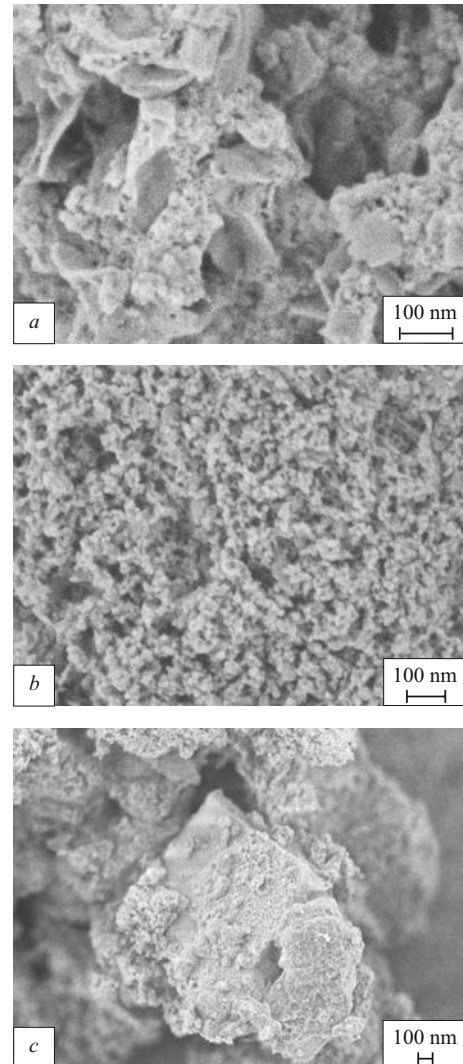


Fig. 1. Individual particles of the synthesized powders I (a), II (b), and III (c).

A JSM-7401F scanning electron microscope (Jeol Company) was used to obtain the photographs for studying the morphology of the powders.

The results of the elemental analysis showed that the precipitation completeness of the components is high for the three precipitation schemes used. Table 1 gives the content of the main oxides, calculated on the basis of the analytical data obtained.

A qualitative analysis of the phase composition of the samples showed that irrespective of the precipitation method the main crystalline phase of the synthesized powders heat-treated at 950°C is pseudocubic, corresponding to a solid solution based on ZrO₂ with fluorite-like structure whose parameter values are presented in Table 2.

The degrees to which the powders are crystallized are close — about 35 wt.%.

The synthesized nanopowders are characterized by the values of the specific surface area presented in Table 3.

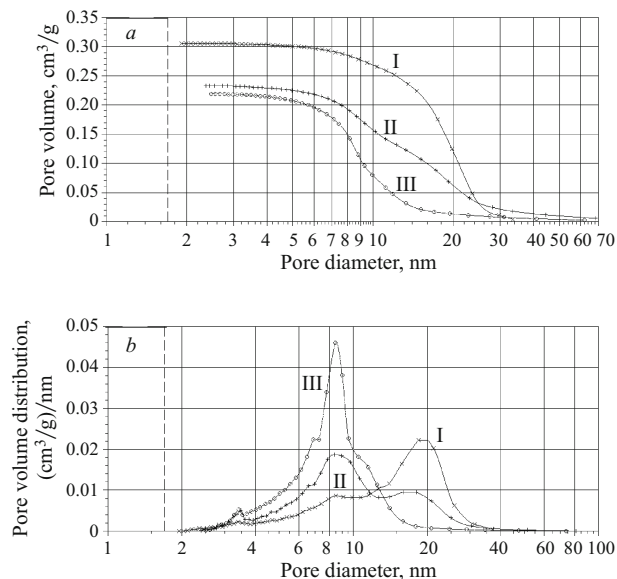


Fig. 2. Integral (a) and differential (b) dependences of the pore volume distribution in the mesopore range as a function of the pore diameter in the synthesized powders I, II, and III. Curves numbers corresponds numbers of powders.

No effect of the precipitation sequence on the specific surface area or phase composition of the powders is observed.

However, the shape of the individual particles as recorded by the electron photographs suggests that the mechanism responsible for the formation of the structure of the powders does depend on the precipitation sequence of the components.

The average computed particle sizes — 17 – 18 nm (see Table 3) — are close to the values measured from the electron photographs — 20 nm (Fig. 1).

The individual particles of the type I powder come in two variants: planar rigid particles about 80 nm in size and globular particles about 20 nm in size. The type II powder consists primarily of particles about 20 nm in size. The agglomerates of the type III powder comprise a more complicated system: the inner component is represented by close-packed amorphized aluminum oxide particles on whose surface are concentrated nanocrystalline particles (about 20 nm), correlated with crystallites of zirconium dioxide which crystallizes in the range 450 – 540°C.

A determination of the porous structure showed substantial differences between the synthesized powders obtained with the precursor components precipitated in different sequences (Fig. 2). The highest porosity is observed in the type I powders obtained with simultaneous precipitation of the components (0.3 cm^3/g), 20 nm pores predominating. The lowest porosity obtains in type III powders and is formed as a result of a large number of very small pores (< 8 nm) which are extremely difficult to remove during sintering [8]. For the type II powders pores smaller than 10 nm predominate but large pores (to 20 nm) are observed.

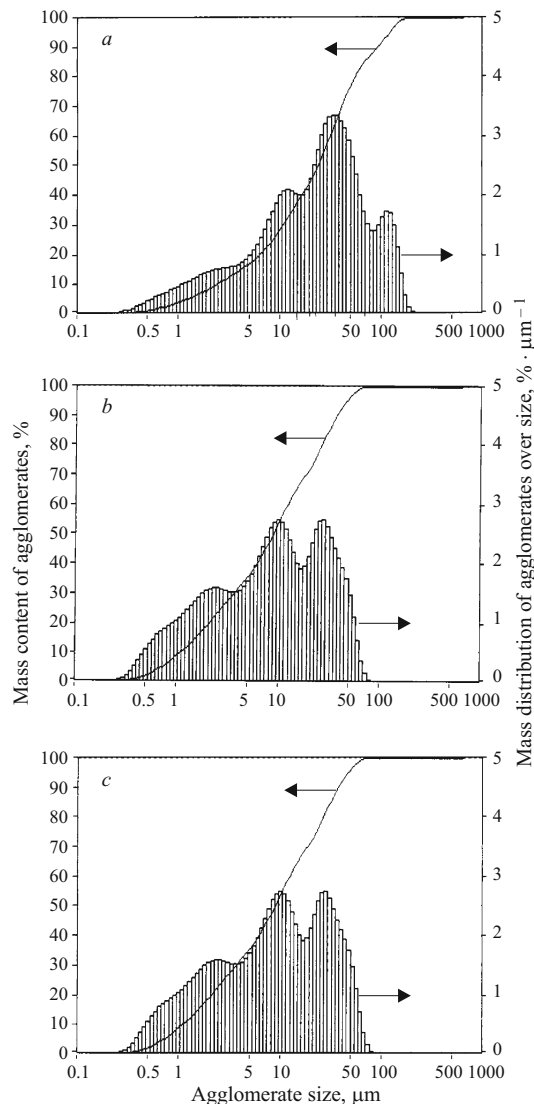


Fig. 3. Integral and differential dependences of the distribution of the agglomerates in the synthesized type I (a), II (b), and III (c) powders.

A high degree of agglomeration of individual nanoparticles is characteristic for powders synthesized from the precursors obtained by the sol – gel method [2]. The synthesized powders are also a system consisting of agglomerates with different size distribution (Fig. 3).

Agglomerates of the type I powder can be represented as uniform with predominate size about 20 μm . For type II powder the agglomerate sizes divide into two types — about 5 and 40 μm . Two types of agglomerates are formed for primary precipitation of the aluminum component (type III powder): small — to 10 μm and large — to 100 μm .

Soft agglomerates slashed by pores of different sizes (10 – 20 nm) are characteristic for type I and II powders, and hard agglomerates, incorporating small pores (about 8 nm), are characteristic for type III powder.

The fact that agglomerates with a definite structure are obtained is explained by the different distribution of the components in the primary precipitate during step-wise precipitation. Specifically, the primary precipitation of amorphized hydrated aluminum hydroxide determines the formation of a dense base of the agglomerate on which subsequently zirconium – cerium hydroxide precipitates, forming a loose surface layer with particles up to 20 nm in size.

Obtaining precursors with different sequences of precipitation of the components of the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{CeO}_2$ by the procedure presented above permits synthesizing powders with a prescribed chemical composition with a large range of particle sizes and individual particle sizes to 20 nm. The morphology of powders and their degree of agglomeration and porous structure depend on the conditions under which the precursors are obtained. Subsequently, this determines the degree to which sintering processes are activated.

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